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THE INFLUENCE OF GREAT EPOCHS OF LIMESTONE FORMATION UPON THE CONSTITUTION OF THE ATMOSPHERE.

THE virtues of carbon dioxide are in inverse ratio to the sinister reputation which "a little knowledge" and a narrow homocentric point of view have given it. As a constituent of the atmosphere it is as necessary to the maintenance of life as oxygen because it is the food of plants and they in turn are the food of animals. Its peculiar competency to retain the heat of the sun renders it a decisive factor in the maintenance of that measurable constancy and geniality of temperature upon which the existence of life depends. It is a leading agency in the disintegration of crystalline rock and is a necessary factor in other geologic changes. It is an essential link in a chain of vital processes which involve all the constituents of the atmosphere. Inherently it may be no more necessary to these processes, save in its thermal nature, than is oxygen, but being the *minimum* factor in the atmosphere it becomes regulative and decisive, because variations in it affect the whole cycle of processes dependent on it, while similar variations in the major constituents may have no appreciable effect. It is the *least* chemical constituent of a mixture that determines the amount of reaction. A loss of nitrogen or oxygen equal to .0003 of the atmosphere would doubtless be wholly inconsequential, while that amount of loss of carbon dioxide would be fatal to life and to many important geologic processes. Oxygen would doubtless become the critical factor if geologic processes in the aggregate consumed it more rapidly than they do carbonic acid. But the reverse seems to be the case now, and it has quite certainly been the case throughout the determinable portion of geologic history. This becomes equally apparent whether we approach the question in the order of the actual processes or the reverse.

Taking the average constitution of the crystalline rocks as a basis, even a rude inspection shows that the consumption of carbon dioxide involved in their decomposition far surpasses the consumption of oxygen.¹ Or, reversing the mode, an estimate of the amounts of carbon dioxide and of oxygen respectively, which would be freed from the sedimentary deposits of the earth if they were again reduced to the condition of silicates analogous to their primitive state shows a like excess of carbon dioxide. From these considerations, which do not need to be given numerical expression, it will be apparent that carbon dioxide has suffered much more consumption in the progress of the geologic ages than has oxygen. That its consumption has surpassed that of nitrogen is too obvious to require argument.

Whatever the original quantitative relations of the atmospheric constituents, the effect of geologic processes has been their reduction to a quantitative order which is inverse to their functional activity. There is hence a preponderance of the inert and relatively non-participant nitrogen, a medium amount of the more active oxygen, and a minimum amount of the most participant element, carbon dioxide.

Now as the activities of the atmospheric constituents are in many respects connected with each other and mutually dependent, it is obvious that the factor which is at once minimum in quantity and maximum in participation must necessarily be the critical factor of the atmosphere. It is not too much to say that the whole order of vital procedure is hung preëminently upon the function of carbon dioxide as the decisive factor, and it is scarcely too much to say the same of many of the most important of inorganic processes.

The chief reservoir of available carbon dioxide on the sur-

¹ The amount of carbon dioxide which crystalline rocks hold in their microscopic cavities, recently shown by Tilden to be considerable, is only a small fraction of what is required for the carbonation of the rock containing it, on the average. We cannot look to this as a source of enrichment of the atmosphere so far as the superficial rocks which undergo chemical decomposition are concerned, though it may be an important source of enrichment when freed from the deeper rocks by the processes of vulcanism and by other means.

face of the earth is not, however, the atmosphere but the ocean. Reservoir in the ulterior sense is not meant, but in the immediately available sense. I entertain the hypothesis that the interior of the earth is the chief terrestrial reservoir of carbon dioxide in the ulterior sense, and that it is a leading source of secular supply. If Tilden's recent analyses of the carbon dioxide stored in the microscopic pores of rocks, or otherwise occluded within them, be representative of the whole interior of the earth, the total mass of carbon dioxide stored within is something prodigious.¹ To how great an extent this is given forth from age to age and becomes a source of atmospheric supply cannot be determined from present data, but I am fully persuaded that the subject is one of the most vital which now invites investigation. The possible feeding of the atmosphere from cosmic sources also invites definite inquiry. But these are ulterior sources of supply of a secular nature and lie apart from the immediate question here discussed. This incidental mention may serve to definitely set them aside and to forestall misunderstanding.

For the purposes of this paper it is assumed that the constituents of the atmosphere and of the ocean have been essentially the same as at present, and no ulterior source of supply or of loss is taken into account. The endeavor here is merely to trace the effects of a great epoch of limestone formation upon such an atmosphere as we now have, attended by an ocean similar to the present one, and with land relations such as accompany great limestone-forming epochs and their antitheses.

A computation of the approximate amount of available carbon dioxide in the present ocean, based upon the observations of the Challenger Expedition as elaborated by Dittmar, shows a content of about eighteen times that contained in the present atmosphere. This embraces only the carbon dioxide held in the two states familiarly known as "free" and "loose;" that is, (1) carbon dioxide which is simply held in solution, and

¹ On the Gases enclosed in Crystalline Rocks and Minerals. By W. A. Tilden. *Chemical News*, April 9, 1897.

(2) that which constitutes the second equivalent of the bicarbonates—essentially the bicarbonate of lime. The estimate does not include the carbon dioxide which is united with the basic oxides to form monocarbonates and which may be said to be fixed. To put the matter in another form, only that carbon dioxide enters into the computation which separates from the sea water upon evaporation.

According to the old method of interpreting analyses the carbonate of lime present in sea water should all be bicarbonate. It appears, however, from Dittmar's investigations that the amount of "loose" carbon dioxide in the ocean is only about one-half what would be required if all the carbonate of lime (interpreted under the old system) were bicarbonate. The proportions are about as though the lime existed in the state of a sesquicarbonate—a compound of doubtful existence. Under modern methods of interpretation this lower proportion is theoretically explicable, for each of the basic oxides in the sea water enters transiently into combination with each of the acids, and a larger proportion of monocarbonates is thus consistent with solubility, and, in addition, free ions of both oxides and acids are concurrently present. Under this system of interpretation the proportion of carbon dioxide necessary to maintain the lime in a state of solution is reduced. In accordance with these direct determinations it will be assumed in the discussion that the "loose" equivalent of carbon dioxide is only half the amount necessary to render the carbonate of lime a bicarbonate. It is by no means certain that under the conditions of an atmosphere rich in carbon dioxide the amount would not reach the full second equivalent required by the old chemical philosophy, but the more conservative basis serves equally well the purposes of this discussion.[†]

Data are lacking for more than a very rude approximation to the amount of free carbon dioxide held in simple solution in the ocean, but such data as are available seem to indicate that it

[†] The elaborate investigations of Treadwell and Renter (*Zeitsch. Anorg.* XVII, p. 170) indicate that the lime is essentially bicarbonate so far as it is carbonate at all.

probably does not exceed two or three times the amount held in the atmosphere. If we assume these figures to be approximately correct there remains, in a semi-fixed or loose condition, carbon dioxide to the amount of fifteen or sixteen times the present normal content of the atmosphere. This large reserve of carbon dioxide is the radical factor in this discussion.

Let a status of land and water and of atmosphere and ocean, such as now exist, be assumed. Since a certain amount of carbon dioxide is associated with the monocarbonate of lime in solution as the second or bicarbonating equivalent, and since the secretion and deposition of the lime takes place as the monocarbonate, the associated carbon dioxide is set free. The deposition of limestone is, therefore, a process of conversion of semi-fixed carbon dioxide into free carbon dioxide. This free carbon dioxide under the law of diffusion distributes itself through the ocean and the atmosphere according to the demands of tensional equilibrium. The ocean and the atmosphere are thereby alike enriched in carbonic acid. If this process were continued without reciprocal action of the opposite kind, the ocean would in time be exhausted of its calcium bicarbonate and the semi-fixed factor would all become free.

But as elsewhere urged¹ the disintegration of crystalline rock through the agency of the atmosphere consumes carbon dioxide in the carbonation of the alkalis and alkaline earths contained in them.² In particular, the calcium silicates of the crystalline rocks become calcium bicarbonate and are in part carried in solution down to the ocean. Over against the liberating function of lime-deposition, therefore, there is set this reciprocal process of fixation. Over against the enrichment of the atmosphere in carbon dioxide due to the former there is a depletion due to the latter. Now if these two processes were in perfect balance, a static condition of the atmosphere, so far as these factors are concerned, would be maintained. It is, however,

¹ A Group of Hypotheses Bearing on Climatic Changes, *JOUR. GEOL.*, Vol. V, No. 7, October–November, 1897.

² The organic cycle and other processes affect the supply and loss of carbonic acid concurrently, but they are purposely omitted here for simplicity's sake.

beyond reason and beyond geological evidence to suppose that these are habitually in perfect or even in approximate balance, for at certain stages the exposure of the land has been large and its elevation high and the process of rock disintegration and carbonation has been notably favored. Coincident with this the ocean has at such times been extensively withdrawn from the continental platforms and the previous expanse of lime-depositing areas thereby greatly circumscribed. In addition to this, the rejuvenation of the streams has at such times brought into the ocean exceptional amounts of detritus and rendered the coasts uncongenial to many of the limestone-forming organisms. It is probable also that even the pelagic calcareous organisms have been at such times adversely affected directly or indirectly by these conditions. On the other hand there have been times when the sea crept out over great areas of the continental platforms and afforded vast expanses of shallow water congenial to the maintenance of lime-depositing life. There is direct palæontological and physical evidence that such extensive epicontinental seas were spread upon the eastern and western continents at the same time, as for example, in the Ordovician, the Silurian, the Carboniferous, and the Cretaceous periods. Geological evidence compels us likewise to recognize recurrent fluctuations in the prevalence of such limestone deposition, intermittent with the antithetical process of land degradation.

Returning now to our selected case based on the present status of atmosphere, ocean, land, and water, we may safely assume that one or the other of the two alternatives, the fixation of carbon dioxide, or the freeing of carbon dioxide, is at present preponderant. Either the carbonic consumption upon the land is in excess of the carbonic freeing in the ocean, or the reverse is the case; if not so momentarily, at least so habitually.

Let us assume, in accordance with the probable fact, that the disintegration of the silicates is now exhausting the carbonic acid of the atmosphere faster than the deposition of limestone eliminates it, and that, therefore, the calcium bicarbonate in the ocean is increasing. The result of this process if prolonged

without interference would be the exhaustion of the carbonic acid of the atmosphere, and, incidentally, the lowering of the surface temperature through the withdrawal of the heat-conserving influence of the carbon dioxide, the reduction of the moisture of the atmosphere through the decline of the temperature, the checking of the vegetal growth, and if the process were to proceed to its extreme, the destruction of vegetal life, and of animal life as well. There would also be concurrent diminution of the chemical disintegration of the rock because of the lessened supply of the disintegrating agency, carbon dioxide, and because of the reduction of the auxiliary agencies, warmth, moisture and vegetation. Theoretically, rock disaggregation by physical agencies might grow into relative preponderance over chemical disintegration, since it would be aided by the sharp oscillations of temperature which would follow the withdrawal of the equalizing blanket of carbon dioxide and aqueous vapor. In such a case the land detritus from crystalline areas would constitute arkose deposits which stand in genetic contradistinction to the limestones, mudstones, and sandstones, which are the result of chemical disintegration through the preponderant agencies of carbonic acid and water. Whether this is really the explanation of the arkose deposits that occur at certain geological horizons is not here seriously considered. The assumed procedure is simply carried to its logical extreme. Arkose deposits may certainly be made locally under present conditions.

But the process cannot reasonably be supposed, under current conditions, to go to the ultimate extreme of destroying all life and subjecting the nude surface to mechanical disaggregation; for the process is self-checking. With the reduction of the carbon dioxide in the air, the rate of consumption is decreased as just indicated. At the same time the ocean is being enriched by the calcium bicarbonate carried down by the land waters, and the conditions there rendered more favorable for the formation of limestone and, through it, for the freeing of the second equivalent of carbonic acid. Even if the rate of freeing this

carbonic acid were reduced temporarily by the indirect adverse influences springing from the impoverishment of the life on the land, the continued reduction of the rate of consumption of carbonic acid on the land must cause it at length to fall below the freeing action in the sea, and the impoverishment of the atmosphere give place to enrichment which would run its course until the preponderance of action was again reversed.

But another element of vital importance enters the problem, the changing attitude of the land and the sea. Such changes may be systematic or adventitious. If they are adventitious the results are beyond easy discussion, but adventitious changes are believed to be subordinate to the systematic changes, since these latter follow (1) from coördinate movements of the earth's crust; (2) from uncoördinate movements of the crust which the ocean coördinates by its leveling function, and (3) from no movements at all. The last is the simplest and most representative case.

Let there be no essential movement of the crust for a prolonged period. That this has been an actual case repeatedly, the base levels of different periods testify. During such a period the height and the area of the land are both diminished. The rate of disintegration of the rocks is consequently reduced, and, concurrently, the rate of impoverishment of the atmosphere in respect to carbonic acid and of the conveyance of calcium bicarbonate to the ocean¹ is also diminished. At the same time the edge of the sea is advancing upon the borders of the land, partly by erosion, partly by the lifting of the sea level by the reception of sediments, and partly, perhaps, by the quasi-fluent creep of the continent toward isostatic equilibrium.² This results in the extension of the sea shelf and possibly in the formation of interior epicontinental seas, as exemplified notably in the central epochs of the Ordovician, Silurian, Devonian, Carboniferous, and Cretaceous periods. This extended sea shelf and these epi-

¹ The Ulterior Basis for the Classification of Geologic Time Divisions. *JOUR. GEOL.*, Vol. VI, No. 5, 1898.

² *Loc. cit.*

continental seas furnish conditions congenial to the chief lime-secreting organisms. Preëminently is this true when approximate base leveling attends the wide transgression of the sea, as it normally does, since the two conditions are cogenetic. At such times the waters are relatively free from land wash, and the extended shelves and the epicontinental seas have their greatest availabilities of depth. These are the conditions theoretically most favorable to limestone formation. These seem to be the conditions that actually prevailed at the epochs of great limestone deposition. At such periods great quantities of carbonic acid previously stored in the calcium bicarbonate of the ocean were set free and the atmosphere enriched in carbon dioxide. It was precisely during such periods of special enrichment that the land was most incompetent to impoverish the atmosphere, because it was then smallest and lowest. During the prevalence of these conditions it seems inevitable that the enrichment of the atmosphere should have become notable. A rude computation may give some impression of the quantitative competency of a great deposition of limestone to set carbonic acid free. The limestones of the mid-Ordovician period may be taken as an example. According to the estimate of Dr. Tillo,¹ 17 per cent. of the land is covered by the Palæozoic series and 80 per cent. by the total sedimentary series. Taking no account of the loss by erosion, nor of the portions concealed by the ocean, and making the very conservative assumption that only one-fourth of the sedimentary area is underlain by this wide-spreading formation, and the further excessively conservative assumption that the Ordovician limestones average only fifty feet exclusive of impurities, and that only a half equivalent of carbon dioxide was freed for every equivalent of calcium carbonate extracted from the sea water, we still find the amount of carbon dioxide set free to be sixty times the present carbon dioxide of the atmosphere. It is obvious that this amount could not be extracted from an ocean like the present one without concurrent supply, for it is about four times as great as the ocean's avail-

¹ BERGHAUS' Physical Atlas. Introduction to Geological Maps.

able content. It seems apparent that a process which sets free carbon dioxide in so large a proportion to the total atmospheric content would be competent to vary that content notably, if, as contended, the process is subject to notable variations, and especially if, as also contended, the reciprocating process of fixation varies coincidentally with it so that the two mutually intensify each other's effects.

Dr. Arrhenius¹ has estimated that the addition of two or three times the present amount of carbonic acid to the atmosphere would give the genial climate in the arctic regions which the Tertiary flora indicates. Even if this estimate should be much too small, it would not seem to be beyond the competency of a great limestone-making epoch to enrich the atmosphere in carbonic acid sufficiently to thermally blanket the earth effectively and to so retain, distribute, and equalize the temperature as to render all latitudes available to vegetal and animal life. The notable feature connected with the extension of life to the high latitudes is the marvelous equalization of temperature. White and Schuchert² have recently given great emphasis to this by showing that in the Potomac epoch an almost identical flora flourished in north Greenland and in Virginia. A simple increase of solar heat, distributed as it is today, does not meet the demands of the problem. An equalizing and distributing factor seems to be indicated. And this, eminent physicists from Tyndall to Arrhenius encourage us to believe may be found in a change of the atmospheric constitution in the critical item of carbon dioxide, a change of no excessive amount and without serious variation in other constituents, except as they follow from this incidentally.

If the freeing of carbonic acid incident to limestone deposition were a potential factor in the equalization and amelioration of climate which permitted the extension of warm-temperate life to high latitudes, such extension should be coincident with the great limestone-forming epochs. Such appears to be the

¹ *Phil. Mag.*, S. 5. Vol. XLI, No. 251, April 1896, pp. 237-279.

² *Bull. Geol. Soc. Am.*, Vol. IX, pp. 343-368.

testimony of geological history. It was in the Middle Ordovician, the Middle Silurian, the Middle Carboniferous, the Middle Cretaceous and the early Tertiary that life of the warm temperate types prevailed in the arctic lands. And these seem to be periods of base leveling and of wide incursions of lime-depositing seas. It cannot at present be asserted, on the other hand, that there were intervening periods when warm temperate life did not prevail there, and could not because of low temperature. In the very nature of the hypothesis here entertained, such periods would be coincident with relative land elevation, and their record would be absent, or so obscurely indicated that only critical investigation directed to the point could detect it.

But in the lower latitudes we find evidence of aridity and of cold temperatures intervening between at least some of the periods of extensive limestone formation, as, for example, the saline deposits which took place between the great limestone-forming epoch of the mid-Silurian period and the similar epoch of the Devonian; or, again, the saline and gypsum deposits and red sediments of the Permian and Triassic age between the limestone epoch of the Carboniferous and that of the Jurassic. In this gap also falls perhaps the glaciation of India, Australia, and South Africa. The Pleistocene glaciation and the measurable aridity of recent times, falling between the limestone-forming epoch of the early Tertiary and a possible limestone-forming epoch of the future which should theoretically follow upon the degradation of the continents, if crust movements remain in abeyance, may form another example.

In considering the antithetical epochs where limestone formation is at a minimum, and rock disintegration is at a maximum, it may be noted that at the close of the lime-depositing epoch the ocean is low in calcium bicarbonate and rich in carbonic acid, and is not then predisposed to deposit lime chemically, but is, on the other hand, in a condition to receive and hold the calcium bicarbonate sent down from the land. When, therefore, an epoch of special earth shrinkage and of readjustment to accumulated stress ensues, and the ocean is more fully drawn into the

deepened basins and the land exposed and incidentally corrugated, the conditions for the reversal of the atmospheric change are propitious.

If a computation be made of the amount of carbon dioxide that would be required to disintegrate the crystalline rock requisite to supply the clastic material for a great epoch of sandstone and shale deposition (allowing duly for old clastics used over), a competency to exhaust many atmospheric equivalents of carbonic acid will be shown. This, being correlated with limited limestone formation, and consequent scant returns of carbonic acid from the ocean, seems competent on its side to notably change the constitution of the atmosphere in the direction of poverty of carbonic acid.

The effect of the limestone-depositing epochs upon the atmospheric oxygen and nitrogen has been ignored for simplicity. While doubtless important, the process does not seem to have any such potential consequences as those which attend the decisive and regulative factor carbon dioxide. Its discussion will therefore not be undertaken here.

The action of intercurrent agencies has been purposely ignored. Some of these are quite obvious. The organic cycle of carbonic acid consumption and oxygen liberation by plants, and of carbonic acid production and oxygen consumption by animals, and the coördinate fixation and freeing of nitrogen alternately, was an ever present factor, and contributed in its own way to a constitutional change of the atmosphere. Although the cycle is measurably self-supporting, it is not a solution of the problem of perpetual motion, and the total result for a protracted period is a permanent alteration of the ratios and of the absolute amounts of the constituents of the atmosphere. But the discussion of this is reserved.

The periodicity of epochs of great limestone-formation reciprocating with epochs of great land extension has been assumed on the basis of a recent discussion.¹ That there were intervening

¹ The *Ultior Basis of Time Divisions and the Classification of Geological History*. This magazine, previous number, pp. 449-462.

epochs when neither the one nor the other were greatly preponderant is not only not questioned, but will, in a separate article, be urged as the special agency of an important function in biological, as well as geological, progress.

Other limitations will suggest themselves, as the change of calcium carbonate into calcium sulphate, and the reverse, in the sea or in the course of organic processes, but it is believed that none of them radically affect the particular function herein assigned to great epochs of limestone formation.

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